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IN RE APPLICATION OF: David W. SHEEL, et al.

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FOR: TITANIA COATINGS BY CVD AT ATMOSPHERIC PRESSURE

**REQUEST FOR PRIORITY UNDER 35 U.S.C. 119
AND THE INTERNATIONAL CONVENTION**Commissioner for Patents
Alexandria, Virginia 22313

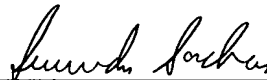
Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

<u>COUNTRY</u>	<u>APPLICATION NO</u>	<u>DAY/MONTH/YEAR</u>
Great Britain	0217553.7	30 July 2002

Certified copies of the corresponding Convention application(s) were submitted to the International Bureau in PCT Application No. PCT/EP03/09314. Receipt of the certified copy(s) by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

Respectfully submitted,
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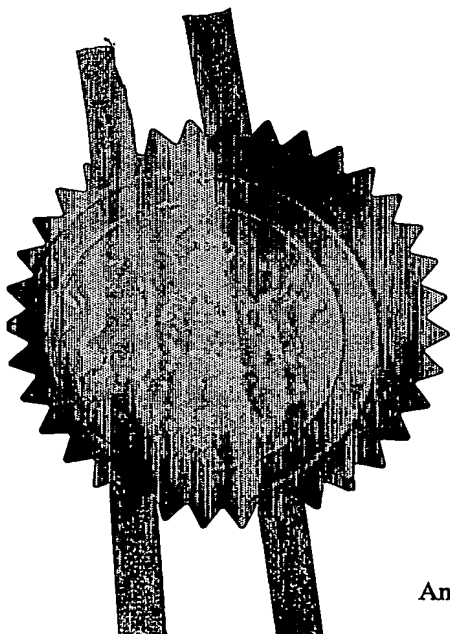
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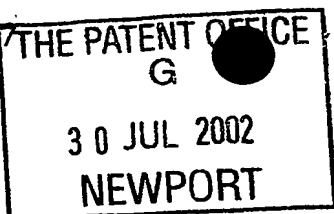
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Titania coating by CVD at atmospheric pressure

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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Titania coatings by CVD at atmospheric pressure

Key words

CVD, Chemical Vapour Deposition, low temperature, plasma, atmospheric pressure, glow discharge, coating, titania, photocatalytic

Abstract

A process is described for deposition of titania, and titania-containing, thin films by CVD, using an atmospheric pressure glow discharge plasma as a major source of reaction, which leads to film properties, and film growth rates, normally only achievable (by atmospheric pressure CVD) with significantly higher substrate temperatures.

Introduction

Titania is a widely used material in thin film coatings. It has been used, for example, as a hard coating and as a transparent dielectric materials in optical stacks. In recent years the photo-catalytic properties of titania have attracted increasing interest. (e.g Paz&luo, J.Mat. Res Vol 10, no11, Nov 1995). Titania layers have been deposited by many techniques (e.g. evaporation, e-beam, sputtering, sol gel, and CVD).

Chemical Vapour Deposition (CVD) has been widely used for many years across a wide range of industrial applications, to produce thin film coatings. In such a process a reactive gas mixture is introduced in the coating region, and a source of energy applied to initiate (or accelerate) a chemical reaction, resulting in the growth of a coating on the target substrate.

Energy sources (for CVD) are normally thermal or plasma, however other sources (such as laser, arc, UV etc) have been employed in special application areas. The choice of thermal or plasma activation is determined by a number of factors – such as film properties required, growth rates, process integration issues, economic considerations etc. However, one primary decision factor is often the operating temperature as defined by the maximum temperature allowed for the chosen substrate. Atmospheric pressure CVD (APCVD) has established itself increasingly in recent years, as a technologically and commercially attractive sub set of CVD coating. It has been particularly successfully employed in high throughput continuous or semi-continuous coating processes. The APCVD approach has also found application in smaller volume processes where its lower overall costs can be decisive. Furthermore, although in many cases the film properties of CVD coatings across many of the deposition activation approaches are broadly similar, there are in certain cases important differences leading to potentially further “differentiated” characteristics of the processes approach.

Such combinations of advantages has lead to AP thermal CVD being used in a wide range of industrial applications such a on-line glass coating, tool coating, ion barrier layer deposition, anti-corrosion and adhesion layers on metals, scratch coatings on bottles etc. An example of AP thermal CVD applied to a continuous process is described in patent no WO 00/705087

As mentioned above, a major limitation to application scope of thermal APCVD has, to date, been the substrate temperature required to achieve target growth rates and target thin film properties. Typically for AP thermal CVD these can be over 500°C and can reach over 1000°C in some applications. A few (APCVD) applications are known which use temperatures below 500°C, for example in the growth of certain II-

VI materials by metal organic CVD, however they are generally limited in scope of application, and apart from the one cited above, tend to produce films with properties sufficient for purpose but not optimised (due to the low temperature requirements). Typically in situations where CVD is the preferred approach but where substrate temperatures are limited to below 500°C and can sometimes be required to be below 100°C, then a plasma approach is often selected. This need for reduced substrate temperatures is also manifested in systems where diffusion processes, which are enhanced at higher temperatures, leads to degradation of the material or device. However, to date such plasmas, used in industrial CVD coating applications, have been based on a vacuum approach.

Such a vacuum approach, although capable of achieving target lower substrate temperatures has major technological limitations for certain applications. The vacuum systems are typically of significant capital cost, and can result in lower growth rates (than APCVD) due to the lower reactive species concentrations in a vacuum. Additionally, vacuum based processes are more difficult to integrate into a high throughput process e.g. requiring complex and expensive handling (e.g. load-lock) approaches between substrate introduction (from open air) into the vacuum system. For continuous strips, films, or sheets this can be a major limitation, and although some solutions have been proposed (based on differential pumping) this is rarely applied due to cost and complexity.

Background to the invention

The described invention addresses the low temperature deposition of titania and also, optionally, a process designed to achieve/retain a degree of photo-catalytic activity. This process seeks to, in part, bridge the significant technological "gap" between current AP thermal CVD and vacuum plasma CVD for the deposition. The invention describes a route to achieving the low substrate temperatures associated with plasma CVD, whilst avoiding the cost and process design constraints of a vacuum system. The invention also allows for much faster titania growth rates to be achieved, than normally possible with vacuum plasma CVD.

Although atmospheric pressure glow discharge plasmas (APGDP) have been known for some time, the application of such plasmas has been largely limited to surface treatment e.g. pre-treatment of plastics prior to printing or second stage coating. In recent years a number of literature reports, and more recently patents, have covered the area of APGDP, their generation, and applications. Patents such as (US 5,938,854 and US 6221268) discuss application to surface treatment. A small number of literature reports cover the issue of using APGD plasmas for producing coatings on a surface. Primarily these are considering deposition of "plasma polymerised" films i.e. films which have a significant organic content or show characteristics which would not normally be considered as inorganic. (e.g. Goosens, Dekempeneer et al, Surface and Coatings Techn, 2001, and DE 19955880). A few patents deal with deposition of inorganic type films (e.g. US 6235647) however the materials considered, and the approaches suggested are not optimised for industrial exploitation. To date no industrial application of APGDP activated CVD is known to us. We are also not aware of any reports of titania deposition via a APGD CVD approach.

The invention described herein addresses these limitations, and defines a process particularly compatible with the establishment of an industrially viable process for the deposition of functional titania coatings.

The process particularly addresses the need for high titania growth rates at lower temperatures than normally employed in APCVD processes. The process also identifies the importance of controlling plasma conditions and gas phase concentrations, to achieve target compositional, physical and functional properties. In order to achieve target low temperature operation and target process characteristics the plasma type and operation details needs to be carefully selected. Many different types of plasmas exist, however a glow discharge plasma is particularly advantageous as it can be operated as a non-thermal plasma. A range of power sources and settings can generate such plasmas, however we have found that the use of low frequency AC plasmas give appropriate performance.

In such a case, where an appropriate plasma is used, the thermal temperature of the plasma is much lower than the electronic temperature. The preferred frequency range for this type of plasma at atmospheric pressure, is different from that normally used for vacuum plasma generation. This can be understood in terms of the generation and trapping of sufficient plasma species, within the plasma-coating zone, which will be moderated by the much higher gas molecule densities at AP. For example, diffusion rates, active species lifetimes and charge build up will all differ markedly with increased pressure operation. The frequency range below 100KHz is typically proposed, and a number of reports use frequencies around 20KHz or below. The optimum frequency will depend a number of factors including; reactor design, materials used, plasma gases chosen, additive concentrations, voltage and power levels employed.

The gases employed to support the GD plasma are normally selected from helium, argon and nitrogen (or mixtures thereof) although it is possible to introduce additional gases as minority components to achieve particular plasma characteristics (e.g. oxidising properties)

To achieve good quality optical and mechanical properties in the films of titania grown using this approach, and also to achieve photo-active titania, we have found it necessary to carefully control the plasma and chemical reactions occurring. An example of this is with water vapour levels in the reaction chamber to avoid unwanted reactions. Careful control of the oxidising source (typically oxygen gas but alternative oxygen containing species can be used e.g. organic oxygen containing species) is necessary to achieve optimum performance in terms of film properties.

Main innovative aspects

The use of an APGD plasma CVD approach for depositing inorganic films is an innovative approach. Achieving good film quality and a viable process is novel. Furthermore, to our knowledge no deposition of titania via a APGD plasma CVD approach has been reported previously. No industrial exploitation of such a process is known. Achieving very high growth rates of good quality films is a major innovative step.

Furthermore, achievement of photo-catalytic film properties via APGD plasma CVD is novel and potentially of significant commercial interest.

Achieving deposition of titania onto plastic films and substrates is a major step forward in opening up commercial opportunities.

To achieve these properties we define a process in which the gas flow through the reaction zone is as close to laminar flow as can be achieved. This requires that a

distributor be employed for the introduction of gases and, preferably, that a further distributor be employed in the extraction region. Furthermore it is necessary that all the reactive gases, to be introduced, are premixed prior to introduction into the reaction zone. It is necessary to choose the plasma type, power, frequency and plasma gas(es) appropriately. We have employed a power supply frequency of 10-25KHz, power levels from less than 1 to around 10 watts per cm². The plasma gases applied have been helium, argon and nitrogen. Helium gives the most stable and flexible configured plasma systems and, generally, the best film quality, however, other gases can be successfully used if design constraints and film property targets are flexible enough. Reactive precursors and oxidising gases have also to be carefully selected for optimum performance. In our work of titania growth, we have employed titanium tetrachloride and alkoxides of titania.

Careful control of the plasma conditions and gaseous composition, during film growth, can be important in achieving a degree of stoichiometric control of the layer composition highly advantageous in achieving desired functional film properties. Achieving this is a balance of having sufficient reaction (e.g. plasma energy, time, oxidation sources, reactive species concentrations etc) to achieve desired chemical and structural properties, whilst avoiding undesirable reactions (e.g. pre-reaction, and enhanced homogeneous reactions)

In our work, we have observed that in order to achieve maximised physical and photo-catalytic properties a post film growth treatment in an APGD plasma produces controllable changes in properties, which are very beneficial. Such changes are believed to be due to bombardment of the grown film with reactive plasma species, which densify, and further react chemically with the film. Surprisingly, we have observed –under certain conditions- a degree of crystallinity or an increase in the degree of crystallinity of the films during this post treatment stage, which is not only helpful for physical properties (adhesion, hardness, scratch resistance, etc) but has a significant impact on photo-catalytic properties. The post treatment stage can be performed in-situ (e.g. by shutting off precursor flow and maintaining a plasma – possibly of different characteristics than that used for growth). It should be noted that films produced by this approach are, however, photo-active even when not showing measurable crystallinity.

Applications

Whilst not wishing to limit the scope, we illustrate the potential of the invention by example.

For coating continuous substrates which move under or through the coating region and where coating at a temperature below that normally applied in thermal CVD is advantageous and atmospheric pressure operation is desired. This can include coating of plastic film, plastic components, continuous or semi-continuous sheets (e.g. of glass, metal, or plastic) and fibres.

Experimental examples

The examples below are meant to illustrate scope, and potential, and are not in themselves meant to be limiting.

Typical experimental conditions applied:

Frequency : 10-25KHz (variable)

Power : 100W to 1 KW.

Configuration : parallel plates with either one or both surfaces covered by an dielectric barrier (e.g. glass, ceramic or plastic film or sheet)

Electrode gap (as measured from the internal surface whether it be the metal electrode or the dielectric) of varied between approx 1 and 15mm. Optimum region was between 2 and 6mm.

Power densities: $0.1 - 10 \text{ Watts cm}^2$ (generally $0.5-2 \text{ watts cm}^2$)

Carrier (i.e. plasma) gas – helium

Carrier Gas temperature (delivered) – ambient to approx 50°C (to ensure precursor volatility)

Plasma gas temperature approx $50-100^\circ\text{C}$ (measured by contact probe)

Carrier Gas flow rate 1-2 litres min

Titania precursor pre-volatilised (e.g. in a bubbler) and delivered at conc. ranges below 1% and most often in the region of 0.1%.

Oxygen level less than 1% and typically less than 0.1%

Photo-catalytic activity measurement

The activity of the films produced has been measured using a series of techniques including stearic acid removal rate, optical scattering reduction, and surface energy measurements. The most commonly applied technique in the literature is stearic acid removal and the experimental procedures are described in a paper by Heller and Paz, J Mat Res vol. 12, no 10, Oct 1997.

In summary, a stearic acid film is deposited on the coating to be tested, and under selected UV irradiation, the reduction in the area of a selected IR peak of stearic acid is monitored as it progressively reduces. In our work we use an FTIR spectrometer to measure this peak.

Analysis instrumentation

Scanning electron microscopy (SEM) images were obtained using a Philips XL30 with Phoenix energy dispersive analysis of X-rays (EDAX) spectrometer. X-ray photoelectron spectra (XPS) were recorded on Kratos Axis 165 or Amicus spectrometers while X-ray diffraction (XRD) data was recorded on a Philips PW1130 diffractometer. Rutherford backscattering (RBS) measurements were made using a 2 MeV accelerator and He^+ analysing beam at normal incidence and scattering angle of 168° in IBM geometry. The RBS data were compared with simulation data from a model using the Quark software package.

Experiment example 1: demonstration of growth rate achievable:

A film of titania was grown from titanium tetrachloride (0.1%) and oxygen (0.1%) in a helium carrier gas. The substrate used was glass. Both uncoated glass and glass which was pre-coated with a blocking silica layer were used. The plasma was initiated in nominally 100% helium, and the premixed reactive gas mixture then introduced. Total gas flow was approx 2 litres per min. Power level was 100Watts over an area of approx 150cm^2 . The configuration was parallel plate with a gap of 4mm and both electrodes covered by a glass dielectric of 2mm thickness. Introduction gas temperature was ambient.

The film was grown over 10 seconds. Gas outlet temperature was approx 80°C . The film grew to a thickness equivalent to growth rate in excess of 100nm per second. The film was measured for photo-activity and found to be photo-catalytically active to stearic acid and contact angle effects. The activity rate (measured spectroscopically by MIR peak area reduction) was estimated at $2.5 \times 10^{-2} \text{ cm}^{-1} \text{ min}^{-1}$ for a film thickness of approx 100nm. The activity level varied with thickness, (as has been

reported in the literature), and significantly higher activity levels of activity were recorded with increased film thickness.

Experiment 2: demonstration of optical properties:

The films produced in example 1 were visually transparent. They were measured on an UV/Vis spectrometer and were found to have high transmission levels across the visible region. Transmission varied with thickness as predicted from reflection related interference effects. Reflection levels from around 12% up to 20% were the film was thickest. Absorption levels were low typically from a few % to less than 1.

Experiment example 3: demonstration of effect of post treatment on properties:

Two films were produced, one as per example 1 and a second produced as per example 1 but then "post treated" by retaining it in the GD plasma for 60 secs. after coating had finished. The resultant films differed notably in properties. The post-treated films were much more adherent and durable (e.g. by cross hatch and water soak resistance tests).

Experiment example 4: demonstration of potential to coat plastics:

The conditions applied to example 1 were then used to coat plastic substrates. Plastics chosen included Perspex, PET and polypropylene. In each case the plastic substrate was pre-treated with the plasma for approx 20 seconds. This pre-treatment was found to enhance adhesion. The films grew similarly to those on glass, and were also found to be photo-active. The films were adherent (to cross hatch) and resistant to abrasion simulation.

Experiment 5: use of alternative plasma gases:

The system used in example 1 was tested for use with alternative (to helium) plasma gases. Argon and nitrogen were used as examples. Argon was the better of the two. The alternative gases could produce a GD plasma but better quality discharges were seen with reduced electrode gaps and thinner dielectrics.

Experiment example 6: effect of oxygen level:

The conditions from example 1 were re-run with varying levels of oxygen. Oxygen was set at 1%, 0.1% and 0.025%.

The experiments were repeated on both glass and plastic substrates. At 1% oxygen the film grew rapidly but with a degree of hazy and pre-reaction which was detrimental to the optical properties of the film produced. At 0.1% the growth rate was comparably high, and the pre-reaction was reduced significantly. Toward the back end of the reactor some more hazy film was noted. If the total gas flow was increased (e.g. to double) this was significantly reduced but at the expense of reduced growth rate and precursor efficiency. At 0.25% the growth rate was reduced by approx 25-50% but the films were of high quality optically and had good adhesion (cross hatch test and after water soaking for 2 hours)

The results on glass and plastic showed similar trends.

Experiment example 7: effect of background water:

Helium was introduced into the reactor with levels of humidity deliberately set at approx 1% and at 0.05%. At the higher level the plasma was unstable and of reduced quality as determined by a visual inspection of the plasma region. No film growth was attempted. At the lower level a significant degree of gaseous pre-reaction was

observed. The resultant film was hazy and of reduced adhesion. When the humidity levels were returned to example 1 conditions (i.e. some tens of ppm) the films returned to good quality.

Experiment example 6: use of alternative precursor:

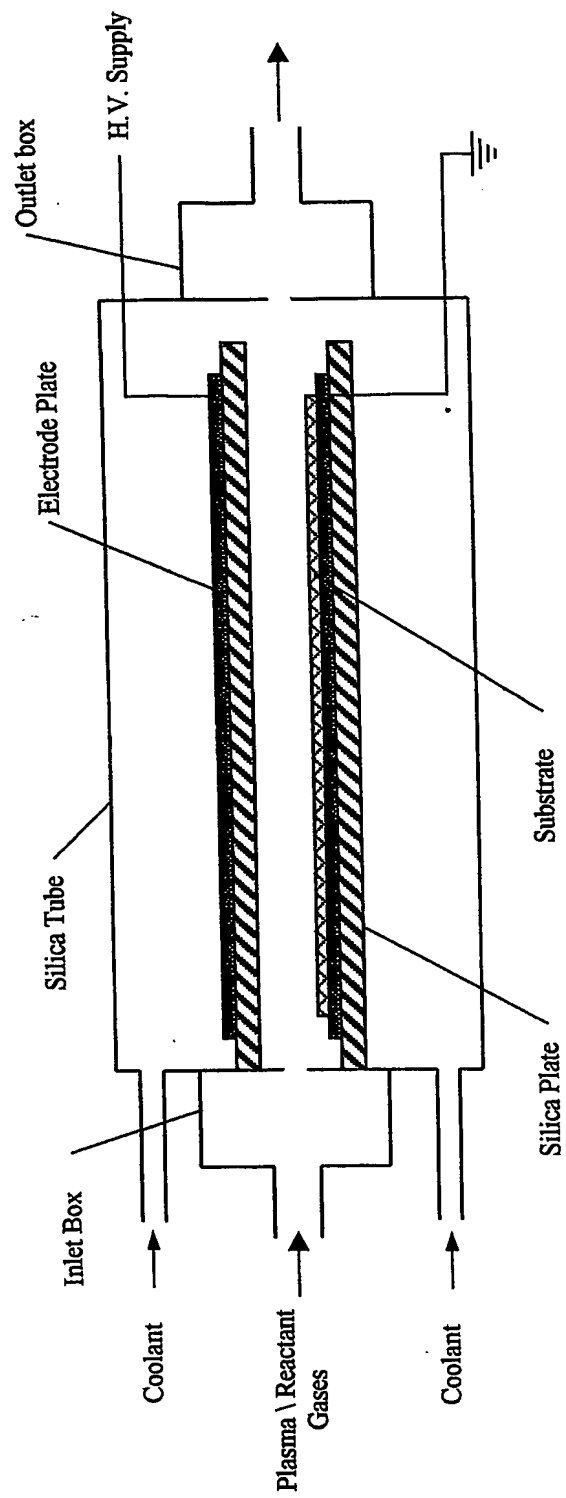
As an example of an alternative precursor (to titanium tetrachloride) titanium tetraisopropoxide was tested. The conditions of example 1 were employed except that no oxygen was used as the precursor contains sufficient oxygen for reaction. The precursor concentration were set at the same level as titanium tetrachloride in example 1. Again a titania film grew quickly and of good quality.

Claims

1. A process for depositing titania, and titania-containing, thin films by CVD, using an atmospheric pressure glow discharge plasma as a major source of reaction, to achieve film properties, and film growth rates, normally only achievable (by atmospheric pressure CVD) with significantly higher substrate temperatures.
2. A process according to claim 1 which is capable of CVD coating at much lower temperatures than those normally associated with atmospheric CVD processes. Substrate temperatures to be below 250°C and, (where advantageous to the process) below 100°C.
3. A process according to claim 1 where the films are photo-active, demonstrated by their ability to destroy organic materials on the surface and/or to modify the surface energy (wetting properties) on irradiation with UV or (selected wavelength) visible light.
4. A process according to claim 1 which, by careful control of the plasma conditions and gaseous composition, during film growth, is capable of achieving a degree control of stoichiometric control of the layer composition highly advantageous in achieving desired functional film properties such as electrical and optical properties.
5. A process according to claim 1 where post treatment of the coating with an atmospheric GD plasma modifies the film properties and structure.
6. A process according to claim 5 where the GD post treatment modifies the film stoichiometry allowing control of film properties).
7. A process according to claim 6 can introduce a degree of crystallinity (primarily anatase)
8. A process according to claim 1 capable of achieving very high growth rates (peak static equivalent), at least 10 nm per second, and up to several tens of nm per second, and (depending on process conditions, product targets and coating materials) peak growth of over 100nm per second.
9. A process according to claim 1 where the films deposited are capable of exhibiting a degree of inorganic composition more normally associated with those produced by thermal CVD where substrate temperatures would be normally at least 100°C (and more typically several hundred degrees) above that employed in this process.
10. A process according to claim 1 which is capable of producing films of good optical quality suitable, for example, for use on substrates which are required to be substantially transparent to the human eye and to be looked through.
11. A process according to claim 1 which is capable of coating preformed and/or thermally toughened substrates

12. A process according to claim 1 where the gas flow into, and through, the reaction zone, and is substantially laminar.
13. A process according to claim 12 which employs an extraction system designed to control gas flow through the coating zone which supports controlled flow
14. A process according to claim 12 where cooling is designed into the coating system to maintain the substrate temperature at the desired level. Such cooling can be achieved by a range of techniques including gas or water or liquid coolant based cooling, or combinations thereof.
15. A process according to claim 1 where cooling is designed into the coating system to reduce unwanted side reactions and to maintain the substrate temperature at the desired level
16. A process according to claim 1, which is capable of coating a wide range of temperature sensitive substrates including thermally preformed substrates and plastic substrate materials.
17. A process according to claim 1 in which a reactive titania CVD precursor is introduced into the gas flowing through the coating region which has been pre-vapourised into the introduced gas flow.
18. A process according to claim 17 in which a reactive titania CVD precursor is titanium tetrachloride.
19. A process according to claim 1 in which a reactive titania CVD precursor is an alkoxide of titanium.
20. A process according to claim 1 in which the level of water and oxygen are controlled carefully to achieve target growth rates and to control unwanted side reactions. The oxygen level is below 5% (of total gas volume) and more preferably below 1%. The water vapour levels are controlled preferably below 1% and more preferably below 0.1%
21. A process according to claim 1 which is particularly suitable for coating moving substrates – both as continuous film or sheet, or a series of substrates supplied semi-continuously.
22. A process according to claim 21 which employs one or more gas flushing zones to allow the introduction, and removal, of the substrates whilst maintaining the integrity of the coating region gas composition.
23. A process according to claim 1 where films can be deposited with a uniformity of at least $\pm 20\%$ and preferably a uniformity of at least $\pm 10\%$ and more preferably better than $\pm 5\%$.
24. A process according to claim 23 which can be used to build up a thicker layer or layers (if required) by arranging sequential coating regions along the direction of movement of the substrate. Such coatings layers can be of the same material or different materials and may also be deposited using the process described here, or alternative methods, which are applicable.(i.e. a hybrid coating technology process)
25. A process according to claim 1 where the GD plasma is generated by a low frequency e.g. AF or RF source where the frequency is below 100KHz and preferably below 30KHz
26. A process according to claim 1 where the metal electrodes are selected from a material which reduces heat generation
27. A process according to claim 26 where the electrodes are made of brass.
28. A process according to claim 1 where the power density of the plasma is below 5 Wcm^{-2} and preferably below 1 Wcm^{-2} and more preferably below 0.5 Wcm^{-2}

Atmospheric pressure Plasma CVD Reactor



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